Density functional study of excess Fe in $Fe_{1+x}Te$: Magnetism and doping

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The electronic and magnetic properties of the excess Fe in iron telluride $Fe_{(1+x)}Te$ are studied by density functional calculations. We find that the excess Fe occurs with valence near Fe^+ and thus provides electron doping of approximately one carrier per Fe, and furthermore that the excess Fe is strongly magnetic. Thus it will provide local moments that interact with the plane Fe magnetism, and these are expected to persist in phases where the magnetism of the planes is destroyed, for example, by pressure or doping. The results are discussed in the context of superconductivity.

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Recently, iron chalcogenides α-FeSe and α-FeTe, another family of Fe-based superconductors, have been reported.[1–7] The superconducting transition temperature T_c has increased from initial 8 K (Ref. 1) to 14 K (Ref. 6) or 15.2 K (Ref. 3) with appropriate Te substitution and 27 K at high pressures (1.48 GPa).[2] While the presently known maximum critical temperatures are lower than in the Fe-As families,[8–12] this binary system has drawn considerable attention due to the apparent simplicity of the structure, the fact that it is As free and the fact that large crystals of $Fe_{1+x}(Se,Te)$ can be grown enabling detailed characterization by neutron and other measurements. These compounds occur in the α-PbO structure, which consists of a c-axis stack of FeTe sheets, with each sheet consisting a square planar layer of Fe, tetrahedrally coordinated by Te, similar to the FeAs sheets of LaFeAsO or LiFeAs. In fact, from a structural point of view these compounds are very similar to LiFeAs, with As replaced by a chalcogen and the Li replaced by a site with a low partial filling of excess Fe. According to literature, these compounds always form with excess Fe.[13–18]

Electronic structure calculations for the stoichiometric iron chalcogenides, FeX,[19] show electronic structures and Fermi-surface topologies very similar to those of the other Fe-based superconductors.[20–26] There is a general proximity to magnetism, especially in FeTe, as well as a substantially nested Fermi surface, which favors a spin-density wave (SDW) instability at the two-dimensional (2D) (π,π) point. While the mechanism for superconductivity in the Fe-based superconductors is yet to be established, there is a strong association between the occurrence of the SDW and superconductivity in the phase diagrams, with superconductivity generally occurring when the SDW is destroyed either by doping or by pressure. The SDW is observed in most of the undoped Fe-As superconducting materials and is accompanied by a lattice distortion.[27–31] For the chalcogenides, a structural distortion with decreasing temperature was detected in $FeSe_{(1-x)}$ (Ref. 32) and superconductivity was found to be close to magnetic instability in $Fe(Se_{(1-x)}Te_x)_{0.82}$ (the formula does imply chalcogen vacancies but reflects excess Fe).[6] Furthermore, $Fe_{1+x}Te$ is reported as magnetic, with properties depending on stoichiometry in several older papers. Bao *et al.*[18] based on neutron results suggested a more complex incommensurate antiferromagnetic order for the $Fe(Se_{(1-x)}Te_x)$ system than in the Fe-As based SDW phases. On the theoretical side, magnetism driven by Se vacancies,[33] noncollinear,[34] and bicollinear[35] antiferromagnetic states have been suggested. However, experimental evidence for substantial concentrations of chalcogen vacancies or a bicollinear state is presently lacking.

Here we report supercell calculations investigating the role of the excess Fe focusing on $Fe_{1+x}Te$. We find that as might be expected, excess Fe donates charge to the FeTe layers, acting as an electron dopant. Interestingly, it occurs with a valence near Fe^+ with each Fe donating one carrier. Furthermore, there is a very strong tendency toward moment formation on the excess Fe. These moments will then interact with the magnetism of the FeTe layers, perhaps complicating the magnetic order. They would also be expected to persist into the regime where FeTe magnetism is suppressed by doping or pressure, perhaps extending the range of magnetic order in the phase diagram and providing pair breaking in the superconducting state.

The electronic structure and magnetism calculations were performed with the projector augmented wave method[36] as implemented in VASP code.[37,38] The generalized gradient approximation[39] (GGA) was employed for the exchange-correlation functional. A kinetic-energy cutoff of 268 eV and augmentation charge cutoff of 511 eV were used to obtain converged energy (within 1 meV). To simulate the partially occupied excess Fe, we used a 2×2 supercell of α-FeTe (two formulas per cell) with one Fe atom (labeled as Fe_2) placed at the $2c$ $(0.5,0,z)$ site, as shown in Fig. 1. This corresponds to a stoichiometry of $Fe_{1.125}Te$. The experimen-

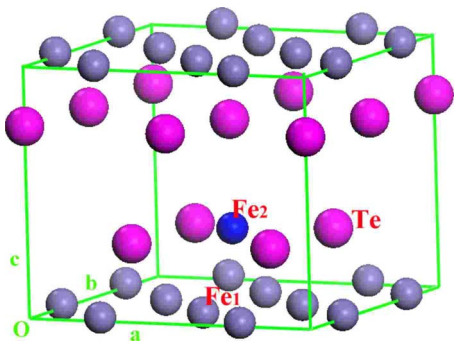

FIG. 1. (Color online) Structure (2×2 supercell of the tetragonal α-FeTe with one excess Fe) used to simulate $Fe_{1.125}Te$ (composition Fe_9Te_8). The iron in Fe-Te layers is denoted as Fe_1 and the excess iron is denoted as Fe_2.

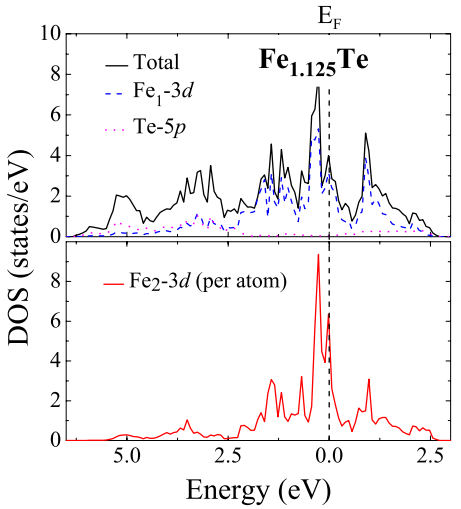

FIG. 2. (Color online) Calculated electronic total and partial DOS for nonpolarized $Fe_{1.125}Te$.

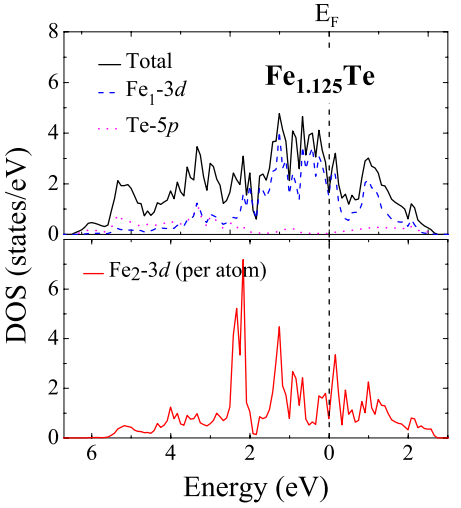

FIG. 3. (Color online) Calculated electronic DOS for $Fe_{1.125}Te$ with the moment formation on the excess Fe_2 (nonmagnetic order for Fe_1 layers).

tal lattice parameters $a=3.8245$ and $c=6.2818$ for $Fe_{1.125}Te$ (Å) (Ref. 17) were used in our calculations. An $8\times8\times10$ grid was used for the k-point sampling of the Brillouin zone, and a denser $16\times16\times20$ k mesh was used for density-of-states (DOS) calculations. The internal coordinates were relaxed to minimize the forces to below 0.01 eV/Å. The calculated coordinate of Fe_2 is $z_{Fe}=0.703$. This is in reasonable agreement with the experimental results in Refs. 14 ($z_{Fe}=0.692$) and 18 ($z_{Fe}=0.721$) but significantly higher than that in Ref. 17 ($z_{Fe}=0.561$).

We begin by showing that the excess Fe atom is strongly magnetic. Figure 2 shows the DOS for $Fe_{1.125}Te$ obtained in a nonmagnetic calculation. The electronic states near the Fermi level (E_F) are mostly of $3d$ character from the Fe_1 layers with a smaller contribution from the excess Fe_2 atom reflecting the low concentration of this site. The result that the Fermi level lies exactly at a sharp peak of the Fe_2 $3d$ DOS indicates the magnetic instability. The calculated Fe_2 partial DOS at E_F is 6.2 states/eV Fe (both spins). Within the Stoner theory the magnetism occurs when $N(E_F)I>1$, where $N(E_F)$ is the DOS at the Fermi level per atom per spin and I is Stoner parameter, typically in the range of 0.7–0.9 eV for Fe. The large Fe_2 $3d$ DOS at E_F easily exceeds the Stoner criterion. Indeed, when allowing spin polarization for the Fe_2 atom (not Fe_1 layers), the total energy is reduced by 48.9 meV as shown in Table I. A pseudogap is opened with the Fermi level falling near its bottom, as shown in Fig. 3. The calculated Fe_2 DOS at the Fermi level is reduced to 0.8 state/eV Fe. The calculated magnetic moment for Fe_2 is $2.5\mu_B$.

This conclusion is robust. For example, addition of on-site Coulomb terms on the Fe_2 site, as in, e.g., GGA+U calculations, would only further favor integer occupation and further stabilize the moment formation. In this regard, however, it is useful to discuss the role of Coulomb correlations in the Fe-based superconductors. First of all, we note that in a Hubbard correlated material such as the undoped cuprates or other Mott insulators, such as NiO, the antiferromagnetic state is insulating and is separated from the conducting doped state by a metal-insulator transition, while in the Fe-based materials, both the magnetic and paramagnetic states are metallic.[40] Furthermore, density functional calculations and calculations with additional on-site interactions, as in the dynamical mean-field theory (DMFT), which is the appropriate extension of the GGA+U method for metals, yield very different electronic spectra.[41] In particular, while density functional calculations do yield some Fe character at binding energies corresponding to the ligand levels due to hybridization, calculations with a Hubbard U predict a very large spectral weight at high binding energy corresponding to the Hubbard bands. This is in disagreement with experimental

TABLE I. Calculated energy difference (in meV/$Fe_{1.125}Te$, relative to the nonmagnetic state for all of Fe) between different types of magnetic arrangements for Fe_1 in layers and excess Fe_2.

	Fe_2 (nonmagnetic)	Fe_2 (magnetic)
Fe_1 (nonmagnetic)	0	−48.9
Fe_1 (ferromagnetic)	−104.9 [a]	−72.0
Fe_1 (checkerboard antiferromagnetic)	−93.1	−151.0
Fe_1 (SDW antiferromagnetic)	−131.0 (−199.6 [b])	−186.7 (−256.6 [b])

[a]Actually, this type of arrangement always converges to an "antiferromagnetic" order with Fe_1 and Fe_2 having opposite spin directions.

[b]The calculated value with relaxed structure when fully considering magnetic orders.

results,[42,43] which support a picture of the electronic structure closer to the density functional predictions and indicate correlations of a different nature from those in cuprates and Mott insulators. While clearly more work is needed to establish the nature of correlations, it would seem that density functional theory provides a useful starting point for understanding the electronic properties of these materials and that this description is not improved by inclusion of additional on-site Coulomb terms.

Based on integration of the partial Fe_2 DOS up to the Fermi level and normalization with the total Fe_2 DOS we find 4.7 electrons in the majority-spin states and 2.2 electrons in the minority-spin states. Thus, the excess Fe occurs as Fe^+ and each excess Fe atom donates approximately one electron to the Fe_1 layer. It may be noted that Fe^+ is a somewhat unusual valence state for stable Fe compounds. Here this state is stabilized because of a balance between the two Fe sites. Specifically, in stoichiometric FeTe, Fe is already divalent, and so the more rapid electron doping that would result if the excess Fe were divalent would lead to a more rapid conversion of the plane Fe toward Fe^+. This balance between low valence states for Fe in the plane and excess positions may be responsible for the fact that the structure does not form at higher excess Fe concentrations.

For undoped FeTe, the Fermi level is located somewhat below the bottom of the pseudogap as shown in Ref. 19. The presence of the excess Fe atoms in $Fe_{1.125}Te$ moves the E_F up, reducing the total DOS at E_F. However, despite the electron doping, the total DOS at E_F remains relatively high (1.8 states/eV Fe), which would still put the $Fe_{1.125}Te$ close to magnetic instabilities. Our calculations show that stripe antiferromagnetic ordering (the SDW type) is most stable compared to the nonmagnetic, ferromagnetic, and the checkerboard antiferromagnetic phases (see Table I) assuming the fixed structure for the nonmagnetic phase in all these calculations. Relaxing the structure for the SDW antiferromagnetic state further lowers the total energy by nearly 70 meV.

The magnetic moment of the Fe_2 is calculated to be $2.4\mu_B$, much higher than that for the Fe_1 layers ($1.6\mu_B - 1.8\mu_B$). The excess Fe's strong magnetism is supported by the recent neutron-scattering experiment.[18] The large local magnetic moment of the excess Fe is expected to persist even if the SDW antiferromagnetic ordering of the Fe layers is suppressed by the doping or pressure, thus causing pair breaking in the superconducting phase.

As we have found in our early work, FeTe has the strongest SDW state in the iron chalcogenide family.[19] This is consistent with experimental observations that the SDW state is maintained up to high excess Fe contents, which as discussed correspond to high doping levels (with x up to 0.125 in the $Fe_{1+x}Te$ systems).[3,18] It should also be noted that the heavy doping corresponds to a large size mismatch between the approximately cylindrical electron and hole Fermi surfaces. The driving force for an itinerant spin-density wave is Fermi-surface nesting. As noted,[19] for a large size mismatch the structure in the susceptibility around (1/2,1/2) will develop a dip at the center, with the maximum therefore moving off center. If the SDW stays stable the ordering vector will then become incommensurate. This apparently is the case in $Fe_{1+x}Te$ and may explain the incommensurate SDW observed in neutron scattering.[18] We note than a noncommensurate SDW can arise simply within this itinerant framework at high doping but would require a complex frustration within a local-moment picture.

Turning to the trends, as noted FeTe has a stronger tendency toward magnetism than FeSe and the arsenides and still shows signatures of spin fluctuations.[19] As such, within a scenario where superconductivity arises from pairing due to spin fluctuations associated with the Fermi-surface nesting, FeTe may have particularly high-temperature superconductivity if the SDW can be suppressed. However, the SDW persists up to high doping levels.[18] A particularly interesting experiment would be then to destroy the SDW by pressure and search for superconductivity in the resulting paramagnetic phase. Furthermore, the fact that the excess Fe in this compound, and presumably the $Fe_{1+x}Se$ and $Fe_{1+x}(Se,Te)$ superconductors, has a local moment in proximity to the Fe layers offers an interesting opportunity for experimental investigation of the interplay between superconductivity and presumably pair breaking magnetic scattering in the Fe superconductors.

The presence of local moments on the excess Fe sites also may be important for magnetic ordering. Assuming that the excess Fe is randomly distributed over the Fe_2 site, the appropriate model would be that of an itinerant magnetic system formed by the Fe layers interacting with randomly distributed local moments. Considering that the Fe_2 is dilute and the results obtained showing interaction between the Fe_1 and Fe_2 systems, one may expect that the coupling to the Fe_2 moments would favor ordering of the Fe_1 planes over a paramagnetic state with strong spin fluctuations. In any case, to summarize we find that the excess Fe in $Fe_{1+x}Te$ is strongly magnetic and is also an electron donor, with each excess Fe atom donating approximately one electron to the Fe layer.

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